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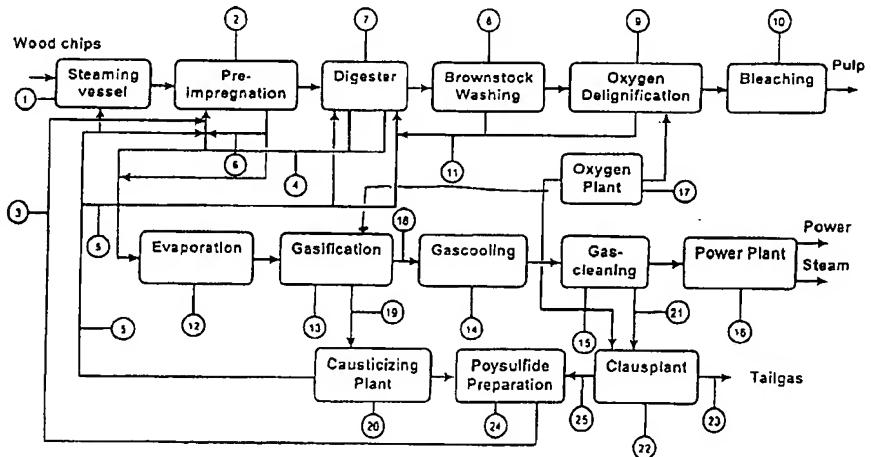
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**(54) Method in connection with Impregnation and digestion of lignocellulosic material**

(57) A method for impregnation and chemical digestion of lignocellulosic material and recovery of pulping liquors. A spent impregnating or cooking liquor is withdrawn and sulphurous compounds are recovered therefrom in a partial oxidation reactor. These sulphurous compounds are converted into hot liquid elemental sulphur which thereafter is mixed with a hot sulphide con-

taining liquor to provide a polysulphide liquor with a concentration greater than 10 g/l and which is essentially free from thiosulphate. This polysulphide liquor is used for carbohydrate stabilising impregnation and/or for cooking at a relatively low temperature.

Fig. 1 Polysulfide Pulping and Chemicals Recovery



EP 0 903 436 A2

**Description****Technical field of the invention**

5 [0001] This invention relates to an improved method for the manufacturing of a chemical pulp from lignocellulosic material using a polysulphide additive preparation to improve delignification selectivity and an efficient method for recovery of the polysulphide additive for recycling. In a specific embodiment the recycled polysulphide additive is admixed with recycled hot black liquor to provide sufficient effective alkali to sustain polysulphide and neutralisation reactions during impregnation of the lignocellulosic material. In another, preferred embodiment, the produced polysulphide is primarily used in a first cooking stage in the digester, which stage is operated at a relatively low temperature. 10 The spent liquor from the digester will then contain large amounts of residual polysulphide which is subsequently used for impregnation of the lignocellulosic material.

**Background of the invention**

15 [0002] In recent years kraft pulping has been subject to great changes. It has been an ambition to extend the delignification in the cooking stage to minimise the delignification work in bleaching operations and to facilitate the replacement of chlorine chemicals. Extended delignification has, however, besides quality aspects, one serious limitation - it decreases the pulp yield.

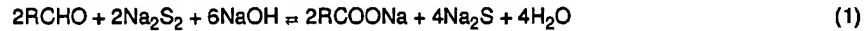
20 [0003] A major part of the yield loss in the kraft process results from alkaline peeling or unzipping reactions of the carbohydrates. Cellulose value is also lost through alkaline extraction and splitting of glycoside linkages reopening sites for secondary peeling. Alkaline extraction takes place even at room temperature but is favoured by increased temperatures and high alkalinity.

[0004] The peeling reactions are automatically stopped during bulk delignification for still unknown reasons, and the 25 cellulose chain is stabilised towards further degradation by alkali.

[0005] The terminal reducing aldehyde group of the hemicellulose and cellulose responsible for the initiation of peeling reactions can be eliminated by means of either reducing or oxidising reactions.

[0006] Polysulphides (PS) in the pulping liquors have been known to stabilise the hemicellulose and cellulose towards 30 peeling reactions by oxidation to a stable carboxyl group with a beneficial effect on overall pulping yield.

[0007] During the polysulphide cook carbonyl end groups in the hemicellulose are oxidised to alkali stable gluconic acid end groups in accordance with:



35 [0008] The reduction in polysaccharide degradation results in a higher yield when pulping is performed to a given kappa number or conversely in a lower kappa number when pulping is performed to a fixed yield. The increased pulp yield in polysulphide kraft processes is mainly a result of glucomannan stabilisation in softwoods and xylan stabilisation in hardwoods.

[0009] Anthraquinone (AQ) addition to PS pulping processes has been shown to be at least additive in its effect of 40 increasing yield and it is conjectured that AQ reduces the thermal decomposition of polysulphide and provides higher carbohydrate stabilization than PS or AQ alone.

[0010] The pulping of wood and other lignocellulosic material using polysulphide liquors is well known in the art and patent literature.

[0011] For example in Clayton et al. US Pat. No. 3,664,919 the PS impregnation is carried out at an application level 45 of 6 percent polysulphide on wood and in Clayton et al. US Pat. No. 3,567,572 a multistep process is described where polysulphide is applied in the absence of alkali.

[0012] In US Pat. No. 4,130,457 a vapour phase polysulphide process is described where pulping is carried out at a low temperature for a short period of time.

[0013] None of these documents describes a practical polysulphide recovery method to be used in conjunction with 50 the pulping process.

[0014] Black liquor oxidation as a means to generate polysulphide in situ in the black liquor for use and recycle to impregnation has been described by Landmark in US Pat No 3,126,887.

[0015] The use of black liquor for impregnation has been practised in mill scale for a long time in batch digester systems and more recently also in continuous digesters.

55 [0016] The use of the effective alkali from spent pulping liquor recycled from the latter parts of the cook to impregnation and initial delignification combined with a high charge of fresh alkali after impregnation was described for soda and kraft pulping already by Sloman in US Pat. No. 2,639,987 in 1953. Black liquor to recovery was extracted after impregnation.

[0017] Up to present time no polysulphide pulping process with optimum stabilising conditions and alkali profile throughout impregnation and cooking with or without recycled liquors has been disclosed in combination with a practical recovery method.

5 [0018] In spite of the lack of practical recovery methods, polysulphide pulping was practised in a few mills in the 1960's by simply adding powdered sulphur to the white liquor:



10 [0019] Although successful in terms of yield gain, this sulphur addition resulted in an intolerable imbalance of sodium and sulphur in the recovery area.

[0020] Until a way to overcome this obstacle could be found, this was not a viable process.

15 [0021] Also US. Pat. No. 3,874,991 describes a process where external sulphur, in a molten state, is added to a combined spent polysulphide solution-hydroxyl ion depleted white liquor together with water and white liquor, if necessary. The resulting polysulphide liquor is used to impregnate the wood chips at a temperature below digestion temperatures, 90 to 140 °C, preferably 100 to 130 °C. This process also suffers from a resulting imbalance between sodium and sulphur.

[0022] Several attempts have been made to generate the polysulphide chemicals from the various forms of sulphur available in the pulping and recovery cycle to avoid the sulphur imbalance obstacle.

20 [0023] For example US Pat. No. 3,331,732 treats green liquor in a scrubber with flue gas. The resulting product is then treated in a stripper to evolve hydrogen sulphide gas which is then treated in a Claus type reactor to produce elemental sulphur.

[0024] US Pat. No. 3,525,666 reuses the sulphur content of black liquor to prepare a white liquor for kraft pulping by carbonating the black liquor to a pH below 11. Hydrogen sulphide gas is stripped and oxidised to sulphur using a Claus process reactor.

25 [0025] In US Pat. No. 3,650,888 a polysulphide recovery process is described comprising vacuum stripping of a carbonated spent liquor to evolve hydrogen sulphide for further conversion to sulphur.

[0026] Common for all processes based on carbonation of pulping liquors to evolve hydrogen sulphide is a high degree of complication including operating difficulties such as encrustation in green liquor pipes and lignin precipitation in the case of black liquor carbonation.

30 [0027] Furthermore, the cost of equipment is high and these polysulphide recovery concepts were never commercialised.

[0028] One step towards introduction of polysulphide pulping into the kraft pulping industry came in the mid seventies as a result of the development of catalysts capable of oxidising some of the sulphur present in white liquor to form polysulphides, thus eliminating the need to add elemental sulphur to kraft liquor to generate the polysulphide sulphur species.

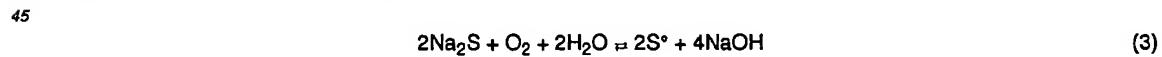
35 [0029] Today at least four processes are available on the market for polysulphide generation by partial oxidation of white liquor.

[0030] US Pat. No. 4,024,229 describes a partial white liquor oxidation process based on air oxidation using a wet proofed activated carbon bed to promote formation of polysulphides.

40 [0031] A similar process based on polysulphide preparation by partial oxidation in a packed bed reactor with small porous active carbon granules is described in US Pat. No. 4,855,123.

[0032] More recently partial white or green liquor oxidation processes have been suggested based on manganese additions to the liquors to enhance partial oxidation selectivity towards polysulphide.

[0033] All partial oxidation processes are based on the same principal chemistry:



[0034] The elemental sulphur then reacts with sodium sulphide to form polysulphide in the white liquor in accordance with reaction 2.

50 [0035] In spite of some initial commercial success the partial oxidation routes suffer from serious disadvantages. Competing side reactions during oxidation resulting in formation of inert thiosulphate cannot be avoided:



55 [0036] A typical polysulphide cooking liquor from a partial white liquor oxidation process comprises at the most 6-10 g/l of active polysulphide sulphur and a significant quantity of thiosulphate. The sulphide "sulphidity" is lowered substantially with a negative impact on pulping performance and product pulp strength properties.

[0037] Furthermore, to achieve any significant yield increase substantially all white (or green) liquor need to be par-

tially oxidised and consequently all effective alkali has to be charged to the digester in combination with the PS sulphur.

[0038] The efficiency of white liquor partial oxidation systems using carbon catalysts decreases as the amount of suspended solids in white (or green) liquor fed to the reactor increases and thus very clear liquors are required.

[0039] It is a major object of the present invention to provide an efficient polysulphide pulping process including a recovery route without the disadvantages inherent in prior art direct sulphur application and partial white liquor oxidation systems.

[0040] It has recently been suggested (SE 9202996, SE-C-500 263) to recover elemental sulphur for polysulphide pulping chemical preparation in connection with gasification of the black liquor. Such a recovery route should avoid all the problems associated with sulphur recovery and polysulphide preparation as discussed above.

[0041] Black liquor gasification processes are described in several patent documents and US Pat. No. 4,808,264 is included here as a reference as a particularly suitable process to be used in connection with the present invention.

#### Detailed description of the Invention

[0042] The pulping of wood and other lignocellulosic materials with polysulphide liquors is well known in the art. Previously mentioned patents describe the advantages obtained from polysulphide pulping and the various methods to recover the active pulping chemicals.

[0043] In accordance with the present invention an improved overall method for chemical digestion of comminuted lignocellulosic material and recovery of pulping liquor including polysulphide is described.

[0044] Specifically, the present pulping and chemicals recovery process according to the basic concept of the invention and a first embodiment involves the following steps:

1) Impregnation of the wood or other lignocellulosic material is carried out in the impregnation zone of a digester or in a preimpregnation vessel, which preferably operates without a counter-current zone, with a first cooking liquor comprising polysulphide in the presence of effective alkali, which alkali has a concentration exceeding 15 g/l as alkali hydroxide.

The temperature during impregnation is kept between 80 - 140 C for a period of from about 20 - 120 minutes. Optionally, excess liquors are removed from the lignocellulosic material after impregnation and recycled and reused, possibly after fortification to the initial polysulphide and effective alkali concentration.

Spent liquor from the impregnation stage can optionally be extracted and removed from the impregnation zone for further processing and recovery of fresh pulping liquor.

The lignocellulosic material and polysulphide pulping liquor preferably pass continuously through the impregnation zone which in one embodiment may be the top portion of a continuous digester. Stabilisation of the carbohydrates by polysulphide is accomplished under the conditions set forth in the following examples by oxidation of the hemicellulose aldehyde end groups to more stable carboxylic groups.

The most notable result of this stabilisation is a higher content of hemicellulose in the product and a higher overall yield.

2) The second cooking liquor introduced after the impregnation zone consists preferably of a low sulphidity white liquor. Cooking is performed in accordance with well known practice to the desired kappa level.

The second cooking liquor should comprise more than 40% and preferably more than 60% of the effective alkali to be charged in the overall delignification process.

The second cooking liquor can be added at various locations during bulk and final delignification and it can be diluted with wash liquor to provide the desired alkalinity and liquor-to-wood ratio.

Apart from the description above, the design and operation of the cooking stages following the impregnation zone are not critical and the overall process described in the present invention may be practised in all modern digester systems including single and dual vessel steam liquor phase and hydraulic continuous digesters as well as modified batch systems. In a specific embodiment of the present invention a

steam vapour phase zone is provided after impregnation to further stabilise the carbohydrates before injection of the second cooking liquor. The material is thereby treated with steam at a temperature of between 130 - 165 °C in a period of between 5 and 30 minutes after the impregnation.

3) The hot spent cooking liquors extracted from the impregnation stage and/or from the downstream extraction screens in the digester are after optional recycling withdrawn for further processing to recover fresh polysulphide cooking chemicals. To prevent undesirable operational problems downstream the digester the residual alkali content in conventional kraft cooking and modified kraft cooking liquor should be kept between six to twelve grams per litre.

Conventionally, spent cooking liquors are combusted in recovery boilers for recovery of the cooking chemicals.

Recovery of chemicals in accordance with conventional practice does not yield the sodium sulphur split necessary to generate the fresh polysulphide cooking liquor for use in accordance with the present invention, whereas emerging recovery technologies based on gasification of the spent pulping liquors have an inherent capability of a sodium sulphur split.

5 4) The spent liquors extracted and withdrawn from the polysulphide pulping method described above are concentrated in a multi-effect evaporator system to a dryness of 65 - 85% and charged into a partial oxidation reactor. Such a reactor and auxiliary system for partial oxidation of spent pulping liquors is for example described in US. Patent No. 4,808,264 which is included here as a reference. Besides recovery of pulping chemicals, a major task for the 10 recovery process is an efficient conversion of the calories in the liquor to steam and power. The combustible fuel gas generated in black liquor gasification processes are advantageously used to fuel a gas turbine power plant.

By controlling the operating conditions in the partial oxidation reactor and by controlled addition of oxygen containing gas, the sodium and sulphur compounds charged with the feed liquor can be split as desired into two separate process streams.

15 The proportion of reduced sulphur in the two streams can for example be controlled by varying the reaction temperature in the reactor and the operating pressure in the reactor. One stream comprising reduced sulphur is accordingly discharged from the reactor in the form of an aqueous solution of sodium sulphide and sodium hydro-sulphide.

20 Another stream, comprising reduced sulphur, is discharged from the reactor in the form of a combustible gas comprising hydrogen sulphide.

If desirable, sulphur compounds may be added to the reactor, preferably as hydrogen sulphide which is recycled from the gasification/gas clean-up system itself, to displace the sulphur chemicals equilibrium in the reactor towards formation of sodium sulphide.

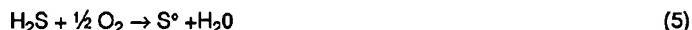
25 Further control of the degree of sodium-to-sulphur split in the reactor could be exerted by adjusting the steam partial pressure in the reactor, i.e. atomising steam, moderator steam, dryness of liquor etc.

The aqueous sulphide containing stream discharged from the reactor is further treated over conventional causticizing to provide low sulphidity white liquor.

30 The combustible gas, comprising hydrogen sulphide, is cooled and transferred to a regenerative gas clean-up system to provide a clean combustible gas and an acidic gas stream comprising hydrogen sulphide and carbon dioxide.

The acidic gas stream is transferred to a Claus plant for recovery of liquid hot elemental sulphur.

35 5) The conversion of acidic gases comprising hydrogen sulphide and carbon dioxide to hot liquid elemental sulphur over the Claus reaction is well known established practice in the chemical and petrochemical industry and a few Claus plants are also in operation in the sulphite pulping industry for recovery of sodium sulphite cooking liquor. Although there are a number of reactions in the conversion of hydrogen sulphide to sulphur, the overall conversion can be represented by



40 Liquid sulphur produced in a Claus plant contains dissolved hydrogen sulphide and hydrogen polysulphides which decompose when the temperature decreases. For this reason liquid sulphur streams are normally degassed before further use.

45 6) In accordance with the present invention we have found that a hot elemental sulphur stream can advantageously be mixed with pulping liquors without any prior degassing under formation of polysulphides and with a minimum of undesirable formation of thiosulphate.

Thiosulphate is an inert in kraft cooking systems and besides the dead load, thiosulphate corrosion have been reported in digesters and impregnation vessels.

50 Prior experiences with sulphur additions to pulping liquors in mills and in laboratories are based on addition of powdered sulphur, with undesirable mixing complications and side reactions with oxygen in the powder bulk.

In the present invention the hot liquid elemental sulphur is discharged directly into the sulphide containing liquor in a closed vessel with a minimum of contact with air or oxygen.

55 The sulphide containing liquor could be selected from white liquor, green liquor or black liquor or a combination thereof. Polysulphide is formed in accordance with reaction (2).

A major advantage with the described polysulphide recovery route besides a low content of inert thiosulphate is that the polysulphide liquor can be prepared at a high concentration and consequently it can be applied as

desired at effective alkali levels optimal for carbohydrate stabilisation.

Preferably, the hot liquid elemental sulphur is admixed with a hot (preferably at least 80 °C) sulphide containing liquor comprising 10-30% of the effective alkali to be charged in the production of chemical pulp.

Polysulphide liquor with a concentration of 10 - 100 gram per litre can be prepared. Preferred ranges are however from 15 - 40 grams litre.

7) Polysulphide liquors prepared in accordance with the present invention can be added to the impregnation zone in combination with other liquors to establish the desired liquor-to-wood ratio and level of effective alkali charge. In a preferred embodiment of the present invention the first cooking liquor used for impregnation of the lignocellulosic material comprises fresh polysulphide liquor and recycled spent liquor from impregnation and /or cooking. The quantities of recycled liquors are selected so as to provide sufficient effective alkali to sustain polysulphide and neutralisation reactions during impregnation and initial delignification and to provide a ratio of pulping liquor to lignocellulosic material of at least 3.5:1.

15 [0045] In addition to the previously known and described yield increase, it has now also been surprisingly found that a significant increase in the delignification rate can be achieved when a large portion of the polysulphide liquor is added to a cooking stage in the digester, meaning that polysulphide is present during the cooking stage. However, to keep polysulphide at a relatively stable condition, the cooking temperature has to be reduced in relation to conventional cooking temperatures. At a lower cooking temperature there will also be a large remaining portion of the polysulphide in the 20 spent cooking liquor. By withdrawing this spent liquor after said cooking stage and introducing it into the impregnation zone, an additional positive effect, that is carbohydrate stabilisation according to previously described principles, will be achieved.

[0046] A preferred embodiment of the invention is based on the surprising discovery that the delignification rate can be increased by polysulphide cooking at relatively low temperatures. In this embodiment of the invention, which is further described in connection with the figures 2 - 4, a delignification increase in the digester is combined with a carbohydrate stabilising effect in the preimpregnation vessel.

[0047] With the foregoing description in mind, a number of drawings are presented which will illustrate the manner in which the invention is carried out. However, these drawings are not to be construed as limiting the scope of the invention in any way but are provided merely to point out the efficacy of the invention in attaining an exemplary economical pulping and recovery scheme and to demonstrate a preferred utility of polysulphide yield enhancement chemicals.

#### BRIEF DESCRIPTION OF THE DRAWING

[0048]

35 Figure 1 is an illustration of the different unit operations in a bleached kraft mill practising polysulphide pulping in accordance with the present invention.

40 Figure 2 shows a continuous two vessel steam/liquid-phase digester arrangement according to a preferred embodiment of the invention.

Figure 3 shows a diagram presenting the difference in the delignification rate with (●) and without (○) polysulphide present during the first 240 minutes of a kraft cook at 147°C.

45 Figure 4 shows a diagram presenting the thermal decomposition of polysulphide during 120 minutes at 140°C.

#### DETAILED DESCRIPTION OF THE DRAWING

[0049]

50 Fig. 1 illustrates the unit operations in a bleached market pulp mill operating in accordance with the present invention.

Wood chips or other comminuted lignocellulosic material are transported to a chip bin and steaming vessel (1), where the material is subjected to steaming at a temperature between 100 and 140 °C in order to remove air from the chip matrix.

55 The steamed chips are discharged from the steaming vessel to a high pressure feeder system which pressurises and transports the chip slurry from the low pressure feed system to the high pressure impregnation vessel (2).

In addition to cooking liquor comprising polysulphide (3), it is beneficial to add recycled spent cooking liquor from

the digester (4) to the impregnation vessel (2). Optionally, also low sulphidity white liquor from the causticising plant (5) and/or recycled impregnation liquor (6) is added to the impregnation vessel.

The impregnated chips are then passed to the upper section of a steam/liquor phase digester (7) where the chips are exposed to steam, raising the temperature to full cooking temperature, that is, a temperature of 135-175 °C, typically between 140 and 160 °C.

Low sulphidity white liquor comprising at least 40% of the effective alkali to be used during impregnation and cooking is added through one or several conduits to the cooking circulations or directly into the digester.

The cooking and delignification reactions are allowed to proceed to a predetermined kappa number, whereafter the cooked chips are discharged from the digester and passed to the brownstock washers (8).

Hot spent cooking liquor (4) is extracted from the digester through extraction screens for recycle to impregnation and /or recovery of fresh cooking chemicals.

After brownstock washing the pulp is further treated in an oxygen delignification reactor (9) and is transferred to a downstream bleach plant (10) to prepare a pulp product with the desired physical properties. The filtrates (11) from the brownstock washers and oxygen delignification stage are recycled to the digester to provide the desired ratio of liquor-to-wood in the digester.

Spent cooking liquor extracted after impregnation and /or from the digester, is after optional use in liquor recycling modes withdrawn to a multi-effect evaporation system (12) and concentrated to a dry solids content of 70-85 %.

The concentrated spent liquor is thereafter directed to a integrated black liquor gasification combined cycle plant (IGCC) for recovery of cooking chemicals and energy. This plant comprises a gasifier (13), a gas cooling system (14), a gas cleaning (15) system and a power generation block (16).

Concentrated black liquor is injected into the gasifier with an oxidant, preferably cryogenic quality oxygen from an adjacent oxygen plant (17). The oxygen sustains the partial oxidation reactions taking place in the reactor which operates at a temperature of 850-1200 °C and at a pressure of 0.5 to 10 Mpa.

The sulphurous chemicals added to the gasifiers are decomposed in the reactor and split into one stream of hydrogen sulphide gas following the fuel gas stream from the gasifier (18) and into another stream as molten sodium sulphide, dissolved and discharged from the reactor vessel as a low sulphidity green liquor (19). The latter stream is directed to a causticising plant (20) to convert the low alkalinity green liquor into high alkalinity white liquor. At least 20 % and preferably about 30 to 60 % of the sulphur charged into the gasifier is recovered as sodium sulphide.

The fuel gas stream comprising the balance of sulphur as hydrogen sulphide is cooled to a temperature below 100 °C and directed to a regenerative gas cleaning system (15) comprising an absorber and a stripper. The fuel gas is cleaned from sulphur compounds and these compounds are recovered in an acidic gas stream (21) comprising hydrogen sulphide and carbon dioxide.

The cleaned fuel gas exiting the absorber is directed to the gas-turbine power plant for recovery of power and steam. The acidic gas is transferred to an oxygen blown Claus plant (22) for recovery of hot liquid elemental sulphur.

The tailgas stream (23) from the Claus plant is discharged to an onsite sulphuric acid plant or to the odour gas handling system of the mill. The temperature of the hot product liquid sulphur stream (25) is kept over 120 °C and it is mixed directly without degassing into a mixing vessel (22) filled with white liquor. The charge of white liquor and elemental sulphur is controlled so as to bring the concentration of polysulphide liquor produced in the mixing vessel to exceed 10 g/l. The strong polysulphide liquor is recycled to the impregnation vessel to complete the circle (3).

Fig. 2 shows a continuous two vessel steam/liquid-phase digester arrangement according to a preferred embodiment of the invention, providing a delignification rate increase by low temperature polysulphide cooking and which may be operated as follows.

In the top of the impregnation vessel (100) there is a screw feeder which makes the chips move slowly downwards in a plug flow trough the impregnation vessel (100) in a liquor-to-wood ratio between 2:1 and 10:1, preferably between 3:1 and 8:1 and more preferably between 4:1 and 7:1. Hot black liquor, which is extracted from the digester, through screen (101), is added, via conduit (102), together with less than 20%, or possibly none, of the polysulphide liquor, which has been prepared according the previous description, via conduit (103), to the top of the impregnation vessel (100). The concentration of polysulphide in the total liquor added through the conduits (102) and (103), at the top of the impregnation vessel should be greater than 2.5 g/l, and the effective alkali (EA as NaOH) concentration should be greater than 15 g/l. Extra alkali, if required, can be added through conduit (112) containing the low sulphidity white liquor. The temperature during the impregnation step should be kept within 80-140°C for a period of about 20-120 minutes. The chips, which has been thoroughly impregnated and partially delignified in the impregnation vessel, are fed to the top of the digester (104) and conveyed into the top separator.

Preferably, a portion of black liquor is withdrawn from the top of the digester and led to evaporation through conduit (105). More than 80% of the polysulphide liquor used in the process, is added to the top of the digester (104), via conduit (107). The polysulphide liquor is preferably heated by means of a heat exchanger (108). The concentration

of polysulphide should be at least 5 g/l and the effective alkali (EA as NaOH) concentration should be greater than 20 g/l. Extra alkali, if required, can be added through conduit (112) containing the low sulphidity white liquor. The chips then move down in zone (B) at a relatively low cooking temperature, i.e. between 120 and 150 °C, preferably between 135 and 148 °C and more preferably between 140 and 145 °C.

The retention time in this first cooking zone should be at least 50 minutes, preferably at least 60 and more preferably 70 minutes. Laboratory tests have shown that the delignification rate is increased when polysulphide is present, see fig 3. The polysulphide is, however, rapidly decomposed at high temperatures generally practised in conventional kraft cooking system, i.e. at 160-170°C. At a temperature of 140°C, however, as much as 50% of the charged polysulphide remains after 120 minutes, see fig 4. The hot black liquor from the digester will, therefore contain a large amount of polysulphides. This black liquor, with released lignin, a relatively high content of effective alkali and remaining polysulphide is withdrawn through the screen (101) and is introduced at the top of the impregnation vessel via conduit (102) as described above. The alkaline content of this withdrawn black liquor (102) would normally exceed 15 g/l. To achieve the desired alkali concentration in a preferred counter-current zone (C) in the digester, low sulphidity white liquor is added in two recirculation lines (110, 111). The alkali concentration demand in the cooking zone (C) is dependent on the desired lignin content of the produced pulp.

[0050] While preferred embodiments and alternatives of the invention have been shown and described it will be understood that they are merely illustrative and that changes may be made without departing from the scope of the invention as claimed.

## Claims

1. A method for chemical digestion of comminuted lignocellulosic material and recovery of pulping liquor comprising the steps of continuously and sequentially:

a) Impregnating said material with a first cooking liquor;

b) Further treating said material with a second cooking liquor in one or more cooking stages;

c) Extracting spent cooking liquor comprising sulphurous compounds from the impregnation stage and/or from one or more of the subsequent cooking stages;

d) Treating at least a portion of said spent liquor following concentration in a partial oxidation reactor and regenerative gas separation system so as to separate evolved sulphur compounds in at least two separate streams, whereas one stream, comprising hydrogen sulphide, is withdrawn from the reactor and further treated to provide an acidic gas stream comprising hydrogen sulphide and carbon dioxide;

e) Converting said acidic gas stream comprising hydrogen sulphide in a reactor to provide a stream of elemental sulphur;

f) Admixing said elemental sulphur stream with a sulphide containing liquor to provide a liquor comprising polysulphide;  
characterised in

that said second cooking liquor in step (b) provides at least 40% of the total effective alkali to be charged in the production of a chemical pulp from said lignocellulosic material;

that said stream of elemental sulphur in step (e) is in a hot liquid state;

that said sulphide containing liquor in step (f) is hot;

that said produced liquor in step (f) has a polysulphide concentration greater than 10 g/l, is essentially free from thiosulphate and contains less than 60% of the effective alkali to be charged in the production of chemical pulp from said lignocellulosic material;

and in that said produced liquor in step (f) is used in step (a) to provide at least a part of said first cooking liquor.

2. A method for chemical digestion of comminuted lignocellulosic material and recovery of pulping liquor comprising the steps of continuously and sequentially:

- a) Impregnating said material with a first cooking liquor;
- 5 b) Further treating said material with a second cooking liquor in one or more cooking stages;
- c) Extracting spent cooking liquor comprising sulphurous compounds from the impregnation stage and/or from one or more of the subsequent cooking stages;
- 10 d) Treating at least a portion of said spent liquor following concentration in a partial oxidation reactor and regenerative gas separation system so as to separate evolved sulphur compounds in at least two separate streams, whereas one stream, comprising hydrogen sulphide, is withdrawn from the reactor and further treated to provide an acidic gas stream comprising hydrogen sulphide and carbon dioxide;

15 e) Converting said acidic gas stream comprising hydrogen sulphide in a reactor to provide a stream of elemental sulphur;

20 f) Admixing said elemental sulphur stream with a sulphide containing liquor to provide a liquor comprising polysulphide;  
characterised in

that said stream of elemental sulphur in step (e) is in a hot liquid state;

25 that said sulphide containing liquor in step (f) is hot;

that said produced liquor in step (f) has a polysulphide concentration greater than 10 g/l and is essentially free from thiosulphate;

30 and in that said produced liquor in step (f) is used in step (b) to provide at least a part of said second cooking liquor in a first cooking stage that is operated at a temperature of 120 - 150 °C, preferably 135 - 148 °C and more preferably 140 - 145 °C.

3. A method according to claim 1 or 2,

35 characterised in that said first cooking liquor in step (a) has an effective alkali concentration greater than 15 g/l, that the temperature during the impregnation is about 80 - 140°C and in that the impregnation step has a duration of about 20 - 120 minutes.

4. A method according to any of the preceding claims,

40 characterised in that extracted spent impregnation liquor from step (c) is transferred to chemicals recovery.

5. A method according to any of the preceding claims,

characterised in that the lignocellulosic material is subjected to steam treatment at a temperature of between 130-165°C in a period of between 5 and 30 minutes after the impregnation in step (a).

45 6. A method according to any of the preceding claims,

characterised in that the lignocellulosic material is subjected to steaming at a temperature between 100-140°C before the impregnation step (a).

50 7. A method according to any of the preceding claims,

characterised in that the conditions in said partial oxidation reactor is selected so that at least 20 percent of the sulphur compounds charged to the reactor is regained and recovered as hydrogen sulphide in the acidic gas stream.

55 8. A method according to any of the preceding claims,

characterised in that the temperature in said reactor is kept between 850 and 1200 °C by controlled addition of an oxygen containing gas.

9. A method according to any of the preceding claims,  
characterised in that said sulphide containing liquor in step (f) has a temperature of at least 80 °C;

5 10. A method according to claim 1,  
characterised in that extracted spent impregnation liquor from step (c) is recycled to step (a).

11. A method according to claim 2,  
characterised in that said first cooking stage has a retention time of at least 50 minutes, preferably at least 60 minutes and more preferably at least 70 minutes.

10 12. A method according to claim 2 or 11,  
characterised in that less than 20% of said polysulphide liquor is added directly to the impregnation step (a).

13. A method according to any one of claims 2, 11 - 12,  
15 characterised in that at least 80% of said polysulphide liquor is added directly, after optional heating, to step (b) to provide all or a part of said second cooking liquor.

14. A method according to any one of claims 2, 11 - 13,  
characterised in that a major part of spent liquor which is extracted from said first cooking stage is recycled to step  
20 (a), in that a second spent liquor is withdrawn at a location upstream of said first cooking stage and in that a major part of said second spent liquor is led to chemicals recovery.

15. A method according to any one of claims 2, 11 - 14,  
characterised in that low sulphidity white liquor is added to one or more cooking stages subsequent to step (b).

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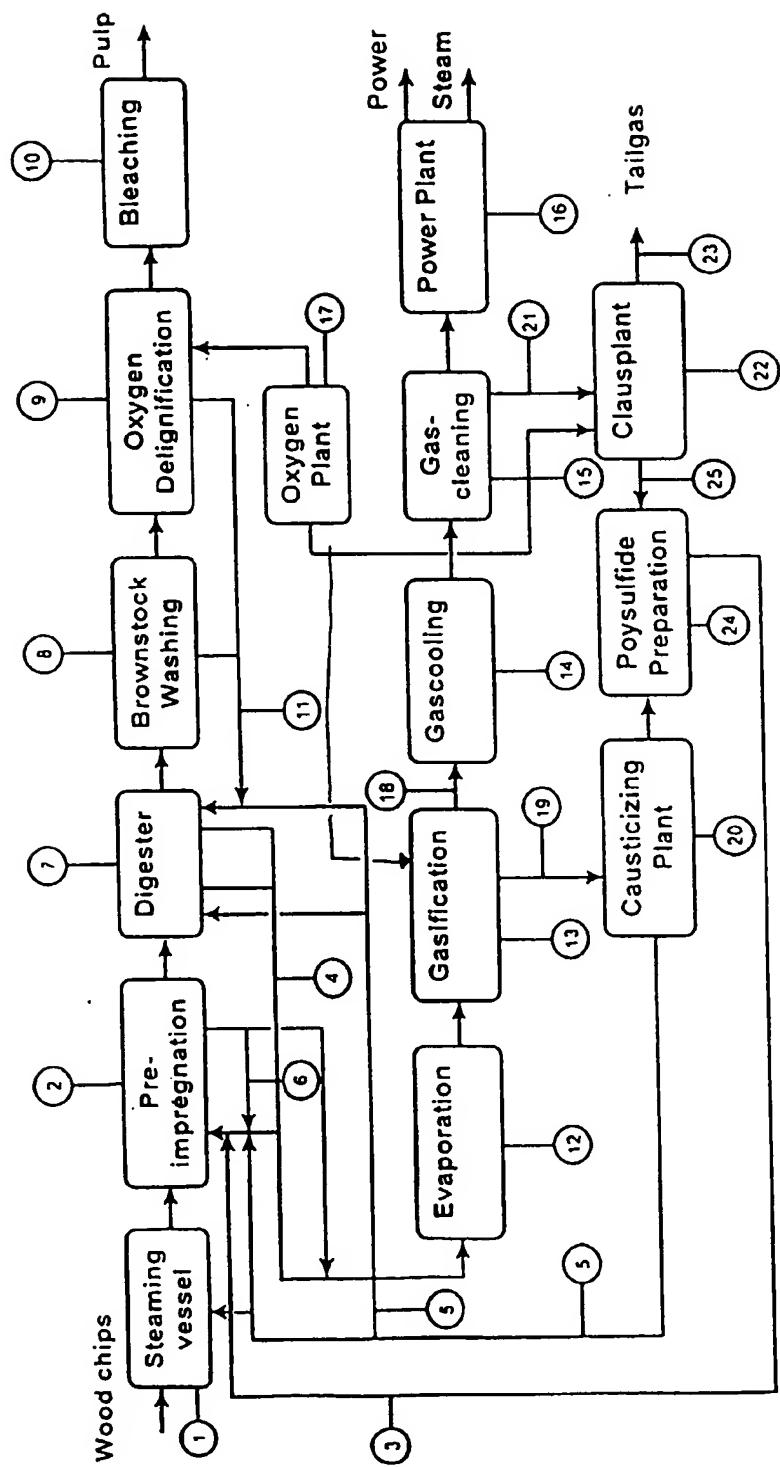
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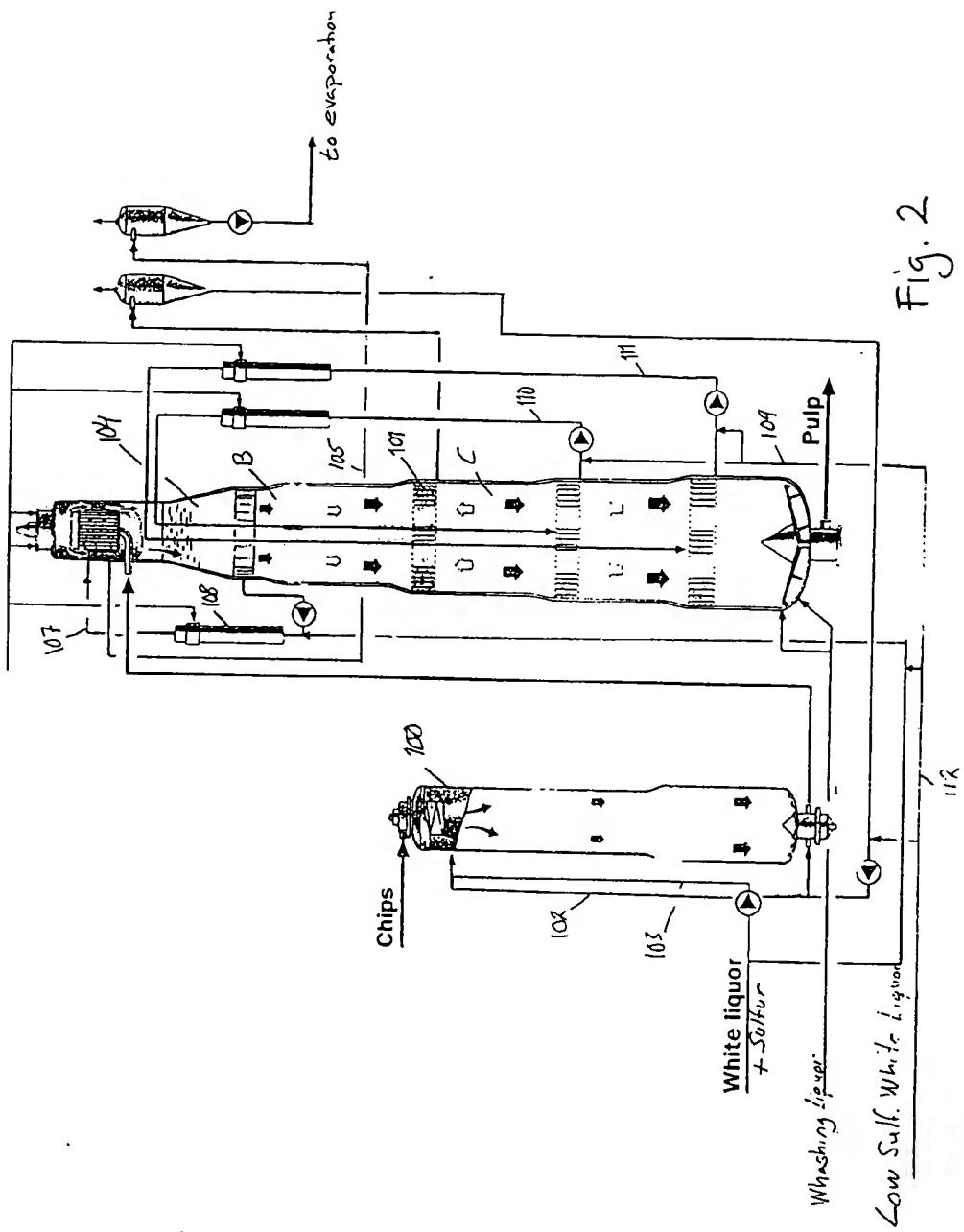
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Fig. 1 Polysulfide Pulping and Chemicals Recovery





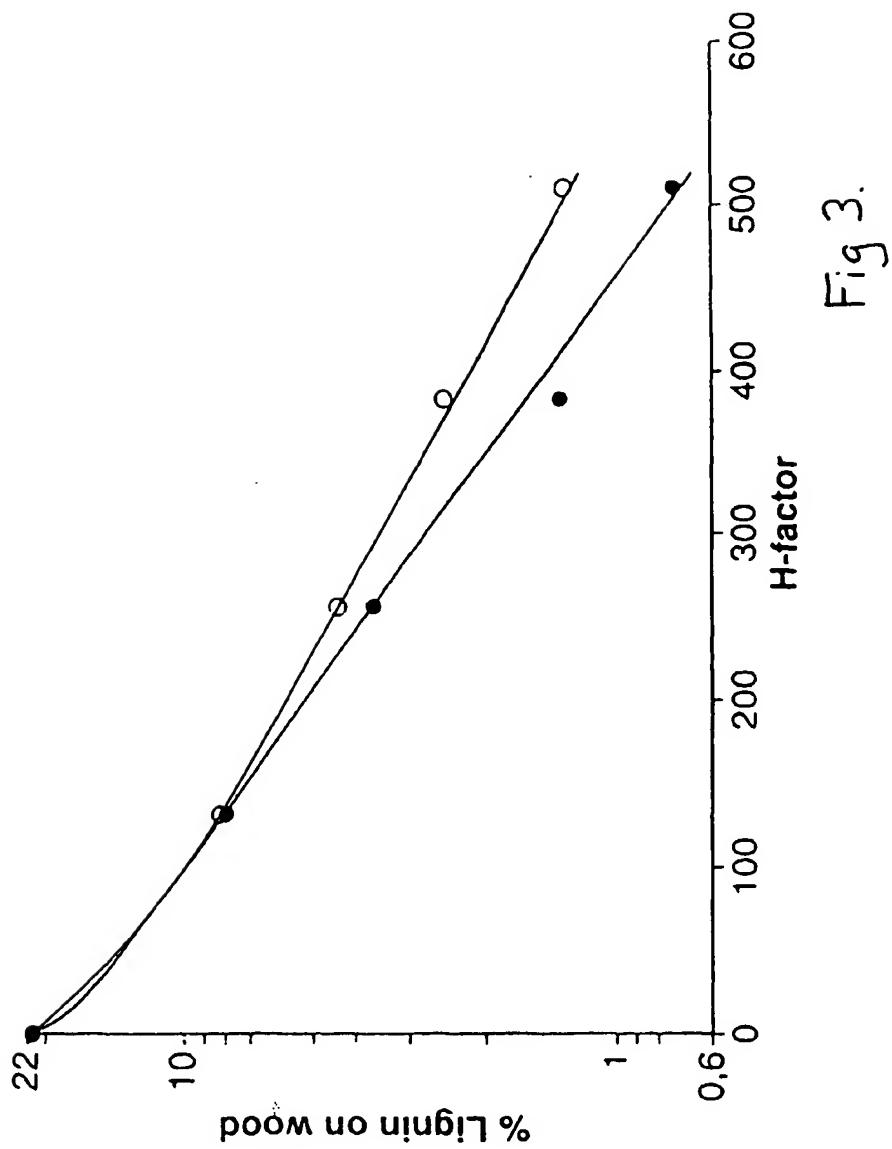


Fig 3.

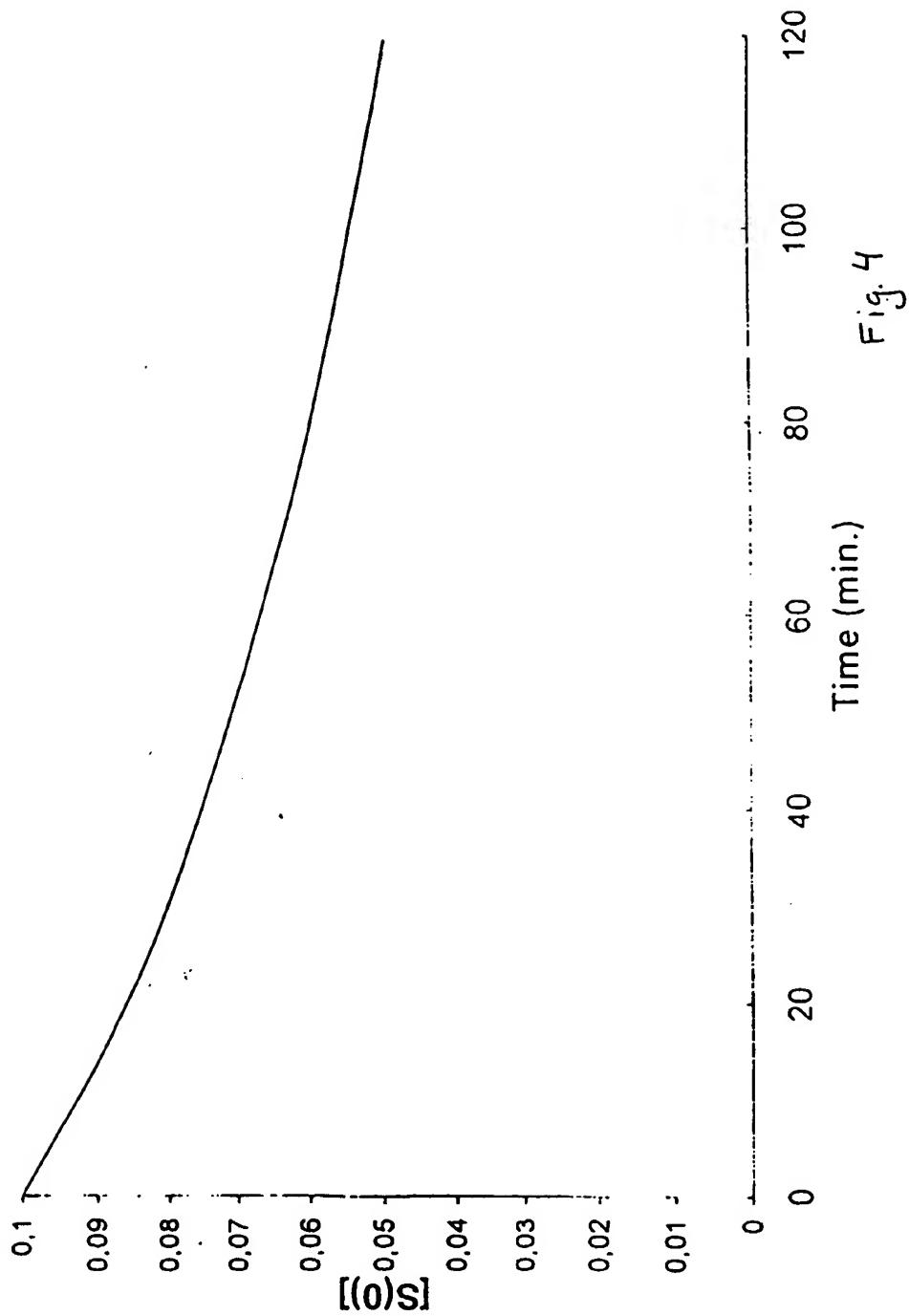


Fig. 4